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Antiferromagnetism in Zn-doped La_2CuO_4 as observed by muon spin resonance spectroscopy

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The local fields seen by positive muons implanted in Zn-doped La_2CuO_4 show a distribution with a main peak attributed to muon sites far from the Zn ions and a satellite structure corresponding to muons residing closer to the Zn. The temperature dependence indicates a strong loss of magnetic order for Cu moments near the Zn atoms. The data can be understood in terms of a model where a Zn ion not only introduces a vacancy in the magnetic Cu lattice but also creates a RKKY-type disturbance. The electron spin polarization around the Zn ions induces a change of the magnetic moments on surrounding Cu ions. The AF lattice is found to be strongly perturbed within a radius of 10 Å around each Zn ion. Possible consequences for the superconductivity of the corresponding Sr-doped materials are discussed.

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I. INTRODUCTION

La_2CuO_4 is, to a first approximation, an insulator where the Cu moments in the $Cu(2)O_2$ planes order antiferromagnetically. It was the base material for the first high temperature superconductors.[1] The material becomes superconducting when holes are introduced into the $Cu(2)O_2$ planes. This can be accomplished by doping with Ba or Sr, although the dopants enter the rare earth site.

One type of experiments that may lead to a better understanding of the cuprate superconductors is the study of effects caused by small changes of chemical composition. It is known that doping of cuprate superconductors with Zn gives a considerably stronger reduction of the superconducting temperature than doping with other impurities, both in the La- and Y-based systems,[2,3] although the doping does not affect the carrier density appreciably.[4] The Zn-effect has been discussed in terms of a destruction by Zn impurities of a possible spin-fluctuation-mediated pairing mechanism.[5] In particular, one experiment has indicated that charge carrier scattering cannot give rise to pair breaking if the interaction is of *s* symmetry, but such a possibility would still exist for *d* waves.[6] In another work,[7] it was concluded that Zn only reduces the mean free path without breaking pairs. Other experimental work on Zn-doped cuprate superconductors include La-NQR studies on Zn-doped La_2CuO_4 (Ref. 8) and Y-NMR on Zn-doped $YBa_2Cu_3O_{6-x}$.[9] In the former, it is argued that T_N decreases with x in a way close to the one expected when diluting a quasi-two-dimensional Heisenberg magnet on a square lattice, while the sublattice magnetization is only slightly affected by Zn doping. In the latter it is stated that Zn increases the magnetic moments of the nearest neighbor Cu ions and therefore causes a relatively strong magnetic perturbation in the AF lattice. For a quantitative explanation in terms of Cu-moment perturbation, these perturbations must, however, be extended relatively far out from the Zn ions.

The magnetic properties of $La_2Cu_{1-x}Zn_xO_4$ have earlier been examined by several groups and with different methods (magnetic susceptibility, neutron scattering, etc.[10,11]). The μSR method provides a measure of the local fields in which the implanted muons precess. In the present work we have used this method, combined with information from susceptibility measurements. For an undoped sample, the low temperature precession frequency is 5.7 MHz, which corresponds to a local field at the muon site of $B_\mu = 42$ mT. This value is in good agreement with calculations using a dipole model assuming that the muons are located at interstitial positions (0.253, 0, 0.162), in lattice units, in the La_2CuO_4 lattice. The Cu ions have magnetic moments of 0.5 μ_B.[12] In the Zn-doped samples, Zn is found to substitute Cu atoms in the $Cu(2)O_2$ plane, thereby removing one Cu moment from the antiferromagnetically ordered lattice. This leads locally to a weakening of the correlation between the nearby Cu moments and thereby to a lowering of the Néel temperature. This should lead to a distribution of fields at the muon sites, with muons implanted close to Zn atoms having local field values B_μ different from those observed for the undoped samples.

The muon experiments were carried out at the μSR surface muon beamline at ISIS, UK, in a zero field setup. We performed a detailed study of the field distribution seen by the implanted muons for different Zn dopings (0–5 at. %) and also studied its variation with temperature up to T_N (see Sec. III). The results are interpreted in terms of a model where the Zn not only removes a Cu moment but also affects the neighboring Cu moments via an RKKY interaction. A similar model was earlier discussed by Walstedt *et al.*[6] for $YBa_2Cu_{2.97}Zn_{0.03}O_{7.0}$ where the Zn also primarily substitutes the Cu in the $Cu(2)O_2$ planes. Possible consequences for the superconductivity of the corresponding (Zn+Sr) -doped compounds are discussed in Section 4.

II. SAMPLE PREPARATION

Samples of the composition $La_2Cu_{1-x}Zn_xO_4$ with x=0, 0.03, 0.05 and 0.07 were prepared by milling appropriate amounts of powders of La_2O_3, CuO (99.9% Johnson Mat-

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TABLE I. Fitted cell parameters for the different compositions at $T=25\,°\mathrm{C}$.

Composition	a(Å)	b(Å)	c(Å)	V(Å^3)
La_2CuO_4	5.3572(4)	5.4051(4)	13.1456(11)	380.65
$La_2Cu_{0.97}Zn_{0.03}O_4$	5.3591(4)	5.4125(5)	13.1313(14)	380.89
$La_2Cu_{0.95}Zn_{0.05}O_4$	5.3640(6)	5.4160(6)	13.1225(18)	381.23
$La_2Cu_{0.93}Zn_{0.07}O_4$	5.3646(5)	5.4214(5)	13.1170(14)	381.48

they) and ZnO (Fotofax) in a Sialon milling medium. Prior to its use, La_2O_3 was heat treated at 1000 °C for 2 h in order to ensure that it did not contain any moisture or OH groups. The powder mixtures were pressed into pellets which were heated in air at 1100 °C for 3 days and this procedure was repeated until single phase samples were obtained (see Table I). The samples obtained were characterized by x-ray powder diffraction with a Guinier-Hägg camera using Cu K_1 radiation and with Si added as internal standard. The films were evaluated with a scanner system.[13]

Single phase samples of the composition $La_2Cu_{1-x}Zn_xO_4$ with $x=0$, 0.03, 0.05, and 0.07 were obtained. The observed unit cell parameters are given in Table I. It can be concluded that a, b, and V increase with increasing x value while the c axis decreases. An increase in the unit cell volume is expected as the ionic radius of the Zn^{2+} is larger than that of Cu^{2+}.

III. MAGNETIC FIELD DISTRIBUTIONS

A. Magnetization measurements

Measurements to determine T_N were first made using a SQUID magnetometer but it was found that the muon data provided more reliable values for the different samples. In Fig. 1 the muon frequency and the normalized damping of the muon signal are shown as functions of temperature. The loss of the precessing signal and the divergence of the damping is a good indication of the ordering temperature T_N.

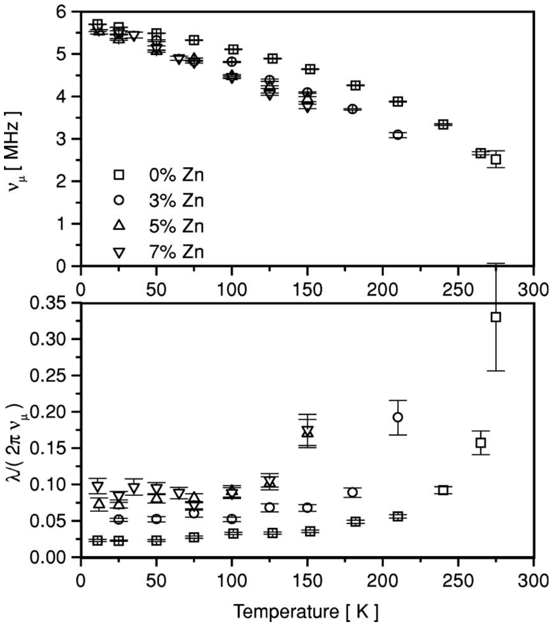

FIG. 1. Muon precession frequencies observed in Zn doped La_2CuO_4 and the corresponding normalized relaxation rates $(\lambda/2\pi\nu_\mu)$.

Assuming that the Néel temperature depends on the Zn concentration x as $T_N(x)/T_N(0)=1\text{-}x/x_c$, our μSR data leads to a critical concentration of $x_c=0.16$, which agrees with earlier published data.[10] This is to be compared with $x_c\approx 0.41$ predicted by percolation theory.[14] These results demonstrate that Zn doping gives a significantly greater effect than the removal of one Cu moment per Zn ion. A first estimate of the effective perturbation radius around each Zn ion can be obtained assuming an even distribution of Zn in the planar AFM lattice of the $Cu(2)O_2$ planes. The Zn ions would then be separated by a distance $r_{\mathrm{eff}}=a\sqrt{1/\pi x}$, where a is the Cu-Cu distance $(=3.779\ \text{Å})$. For $x_c=0.16$, the value of the effective radius, r_{eff}, is $1.4a$ $(\approx 5.3\ \text{Å})$. This value will be further discussed below.

B. Internal magnetic field distributions

A typical time-spectrum in the AF-ordered state is shown in Fig. 2. The spectrum consists essentially of a precessing signal from muons in an ordered magnetic enviroment plus a weakly damped nonprecessing signal. The first fraction of a μs after the proton pulse could not be observed with the present instrumentation, but there is no indication of any fast decaying component in the spectra. The data can therefore to a first approximation be described by a function

$$P(t)=A_p(0)G(t)\cos(\omega\cdot t+\phi)+A_{\mathrm{np}}(t), \tag{1}$$

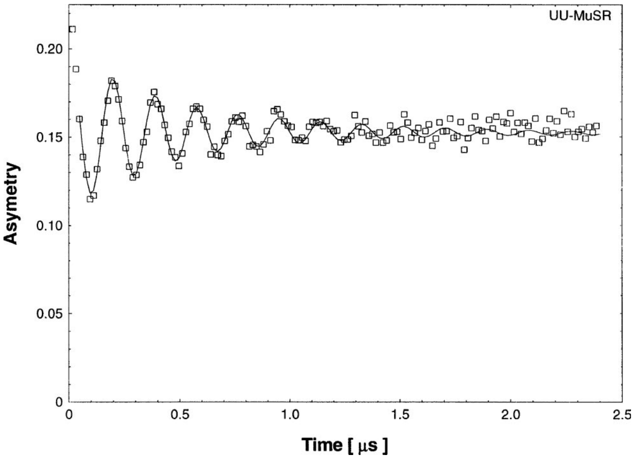

FIG. 2. μSR time spectrum of 3% Zn doped La_2CuO_4 at $T=25$ K.

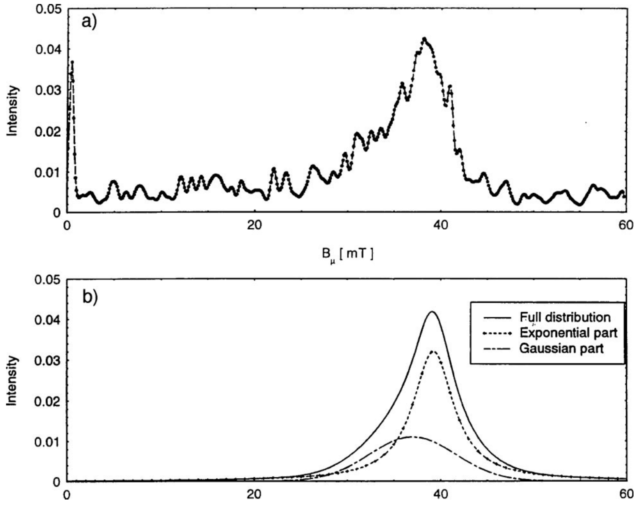

FIG. 3. (a) Distribution of local fields seen by the muon as obtained by maximum entropy analysis for 5% Zn doping at $T = 25$ K. (b) The corresponding distribution obtained by fitting the time spectrum to a two-component function.

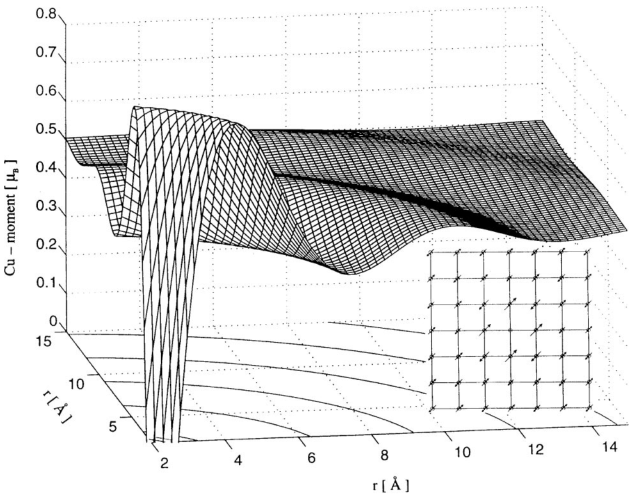

FIG. 4. Calculated magnitudes of Cu moments disturbed by nearby Zn atoms. The calculation was made for 3% Zn. The model is described in the text. The inset is a graphical representation.

where the nonprecessing term $A_{\rm np}$, with only a weak Gaussian relaxation, contains the 1/3 tail of the precessing muons and also the muons implanted in environments with zero local fields. The observed precessing signal $A_p(t)$, which together with its 1/3 tail, constitutes about 50% of the total observable signal, is the part of interest in the following discussion. (The nonprecessing signal is unusually large and so weakly damped that we regard it as originating mainly from muons stopping in the sample environment.)

The precessing component, which at a first glance appears to have one single frequency ω, turns out, on closer analysis to have an asymmetric distribution of frequencies. Such an asymmetric field model is actually theoretically justified in the present situation, as will be shown in Sec. III C. This is also indicated by a frequency analysis using the maximum entropy method,[15] as shown in Fig. 3(a).

μSR allows us, in principle, to obtain a full frequency distribution by Fourier transforming the time spectra, but this would require a data collection time that was not deemed realistic in the present case. Therefore, the data from the Zn-doped samples were first analyzed with one single frequency and then with a two-frequency model. The two-frequency fit should pick up the basics of a model where the randomly distributed Zn ions give rise to a significant change in the Cu moments in their vicinity.

Least square fitting including a second component with a frequency close to the main frequency clearly improves the analysis of the experimental data as seen in Fig. 3(b). They were therefore fitted with the function

$$P(t)=A_1G_1(t)\cos(\omega_1 t+\phi)+A_2G_2(t)\cos(\omega_2 t+\phi)$$
$$+A_{\rm np}(t), \tag{2}$$

where the damping of the "main" frequency (ω_1) signal was best described by an exponential relaxation, $G_1(t)$, while a Gaussian relaxation function, $G_2(t)$, was used for the satellite. The temperature dependence of the main frequency, $\nu_1 = \omega_1/2\pi$, is almost identical with that given in Fig. 1.

C. A theoretical model

Our model is based on the assumption that Zn ions in the Cu(2)O planes not only remove one Cu moment but that they also, via an RKKY-like redistribution of the electron density and spin polarization, cause a change in the moments of neighboring Cu ions. Even if La$_2$CuO$_4$ is expected to be an insulating compound, some degree of electron itineracy has been used for successful modeling in other contexts.[14] Recently it has also been observed, for a similar parent compound of high temperature superconductors (Ca$_2$CuO$_2$Cl$_2$), that a remnant Fermi surface exists, even if the material is considered as a Mott insulator.[16]

For the distribution of the magnitudes of the Cu moments around each Zn ion in the Cu(2)O$_2$ plane we use a modified Kohn-Friedel equation

$$\mu_{\rm Cu}=\mu^0_{\rm Cu}+C_0\frac{\cos(2k_Fr)}{(2k_Fr)^2}, \tag{3}$$

where $\mu^0_{\rm Cu}=0.5\mu_B$. Similar oscillating RKKY terms have been used for instance by Mydosh *et al.*[17] for spin glass systems such as Mn in an Au matrix, but here the situation is reversed since the Zn ions form nonmagnetic perturbation centers in an otherwise perfect magnetic matrix. A simple model of the Fermi surface in the 2D lattice of the Cu(2)O$_2$ planes in La$_2$CuO$_4$ is a square where $|k_x|+|k_y|=\pi/a$. A somewhat more complicated surface was used by Pines[18] for doped La$_2$CuO$_4$. For our simulation we used a constant value of $k_{\rm F}$, which corresponds to a circular Fermi surface.

Using the value $k_{\rm F}=0.6$ Å^{-1} we calculated the Cu moment distribution close to an implanted Zn ion. An example is shown in Fig. 4, for 3% Zn atoms placed randomly in the Cu(2)O$_2$ planes. The resulting field distribution at the muon site (0.253, 0, 0.162) is shown in Fig. 5. It is clearly seen that

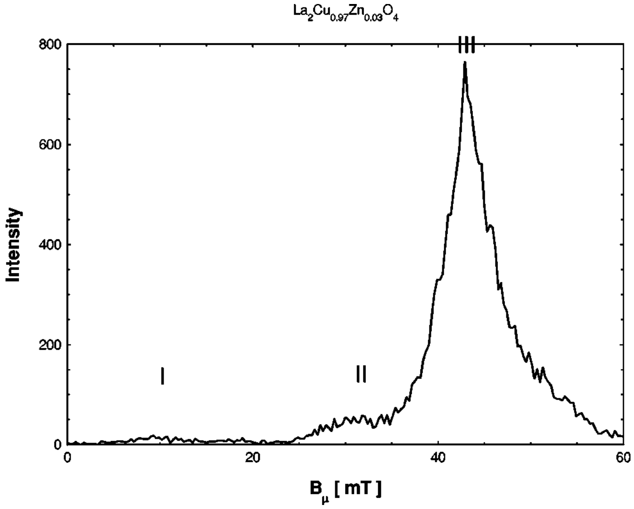

FIG. 5. Calculated distribution of local fields at the muon site in 3% doped La_2CuO_4 obtained with the Cu moments of Fig. 5.

this model predicts a nonsymmetric distribution of fields with the appearance of lower-frequency satellites. The "standard" frequency ω_1, corresponding to a field of 42 mT, is expected to have a main satellite at approximately the position II. The agreement with our data is good. The weak second satellite centered around 10 mT, see Fig. 5, could not be fitted with the present spectra.

The model used here can also be compared with other published data on Zn-doped high-temperature superconductors. The work by Fiorini *et al.*,[10] Corti *et al.*,[8] and Lichti *et al.*[19] refer to the La_2CuO_4 based materials, but it is also relevant to discuss Zn-doping in the $YBaCu_3O_z$ compounds studied by Mahajan *et al.*,[9] Semba *et al.*,[7] Walstedt *et al.*,[6] Mendels *et al.*,[20] and Bernhard *et al.*,[21] since the main effects on magnetism and superconductivity are assumed to stem from changes in the $Cu(2)O_2$ planes which are of similar nature.

From magnetic measurements Fiorini *et al.*[10] found that Zn destabilizes the AF order much more than expected from random dilution and that it induces uncompensated moments in the $Cu(2)O_2$ planes. Both Corti *et al.*,[8] using ^{139}La NMR, and Borsa *et al.*,[22] using μSR found that for $x<0.05$ there are paramagnetic regions around the Zn sites (which appear to freeze into a spin-glass-like state below 100 K). These paramagnetic moments (of total magnitude 0.36 μ_B/Zn ion) were assumed to be induced by perturbation of the AF order on Cu sites close to the Zn ions. A further observation by these authors was that the magnetic correlation length varied only slowly with x, indicating a metallic type of coupling in the $Cu(2)O_2$ planes. In the $YBaCu_3O_z$ system, Walstedt *et al.*[6] studied the ^{63}Cu(2) NMR linewidth and found that it followed a T^{-1} dependence, which would be expected if there is a distribution of Cu(2) moments caused by an RKKY-mediated perturbation. From the measured Curie term in the susceptibility, they derived a paramagnetic moment slightly exceeding 1 μ_B/Zn ion which was assumed to be due to an unbalance in the four nearest neighbor Cu(2) AF-coupled spins. Mahajan *et al.*[9] also attributed the magnetic perturbation to the four NN Cu(2)'s, which corresponded to a total paramagnetic moment of 0.36 μ_B/Zn ion for oxygen content $z=6.92$ and 0.86 μ_B/Zn ion for $z=6.64$. From the frequency shifts and the T_1 relaxation times they concluded that only the Cu moments nearest to the Zn were strongly modified. In an ^{89}Y NMR experiment they could follow the T dependence of the satellites for Y atoms closest to the Zn ions (where they have 5 Cu neighbors, out of which 2 are nearest neighbors of the Zn) and Y atoms at next nearest neighbor positions with respect to Zn.

All the above-mentioned information is consistent with the model presented here, including the applicability of RKKY, as mentioned in Ref. 6. However, most of the cited results refer to effects of Zn on the nearest neighbor Cu sites, whilst the present experiments, which use positive muons as randomly placed magnetic probes, show that Cu moments at considerably larger distances are also perturbed. This is what would be expected when an RKKY-like oscillation of the magnitudes of the Cu moments is imposed on the AF-coupled lattice.

It can be noted that a direct observation of Friedel oscillations near Zn impurities in another (Bi-based) high temperature superconductor has recently been reported.[23]

IV. MAGNETISM AND SUPERCONDUCTIVITY IN La_2CuO_4 BASED MATERIALS

AF fluctuations are now considered to be a main candidate for mediating Cooper pair formation in the high-temperature superconductors (see, for instance, theoretical work by Pines[18] and recent neutron scattering experiments by Tranquada *et al.*[24]). It is therefore of interest to consider the implications of the present results for models based on magnetic fluctuations.

Nachumi *et al.*[25] has studied superconducting $La_{1-x}Sr_xCuO_4$ material doped with Zn to about the same concentrations as in the present study with respect to changes in the superconducting carrier density n_s as a function of increasing Zn content. The variation in n_s can be obtained from μSR experiments by measuring the μSR linewidth $\sigma \propto 1/\lambda^2$ where the penetration length λ can be written as

$$\lambda=(\epsilon_0 m^* c^2/n_s e_{\mathrm{eff}}^2)^{1/2} \tag{4}$$

in the so-called "clean limit" where the coherence length ξ is much shorter than l, the mean free path. Nachumi's results are reproduced in Fig. 6(a). The authors interpret their results in terms of the so-called "Swiss cheese" model, where each Zn ion is supposed to be surrounded by a zone of area $\pi\xi_{ab}^2$ from which superconducting carriers are excluded. Their fit to the data for different Zn dopings [shown as a dotted line in Fig. 6(a)] gives a dead zone radius of $\xi_{ab}\approx 6a$.

A similar calculation [shown in Fig. 6(b)] based on our model shows which fraction of the AF plane that would be allowed if the limit for superconducting carrier transport would be an inhomogeneity $\Delta\mu/\mu$ of 1, 3, 5 or 10% (if large inhomogeneity is allowed, more of the area is available). For agreement with Nachumi's data, a 3% inhomogeneity seems to be sufficient. In our model this corresponds to dead zones with a radius of $6a$ around each Zn ion. These two indepen-

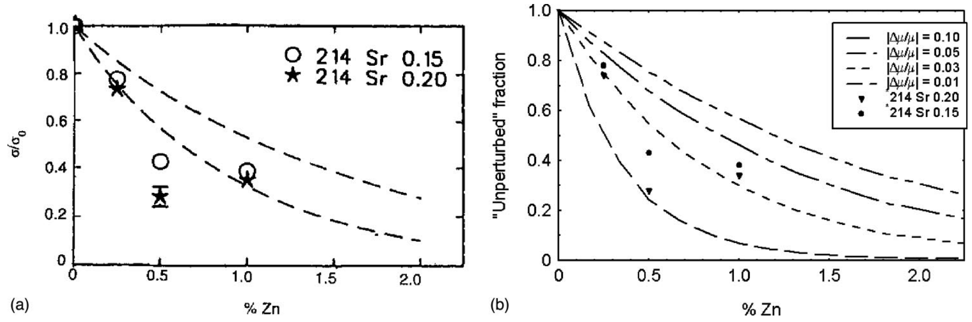

FIG. 6. (a) Influence of Zn doping on the superconducting carriers, $\sigma \propto n_s/m^*$, in La$_{2-x}$Sr$_x$CuO$_4$ [from Nachumi *et al.* (Ref. 25)]. The dashed line is corresponding to a dead zone around each Zn impurity with a fitted radius $6a$. (b) Model calculation of the relative areas in the Cu-O planes that would allow superconductivity if the ''inhomogeneity limits'' are set to $|\Delta\mu/\mu| = 0.10, 0.05, 0.03, 0.01$, dashed curves (from top to bottom). Data points from Ref. 25; see (a).

dently obtained values for the dead zones are in excellent agreement and can be taken as a support for the magnetic carrier mechanism in the high temperature superconductors. If AF fluctuations are involved in the mechanism for superconductivity in the high-temperature superconductors, they must expected to be sensitive to magnetic inhomogeneities. It is known from neutron scattering that AF fluctuations [of sufficient energy to sustain superconducting coupling at temperatures up to ≈ 100 K (Ref. 12)] are still present even in the Sr-doped material, although with short correlation lengths. A basic condition for transport of charge carriers via AF-fluctuations must be that they should not be perturbed locally by an inhomogeneity in the magnetic energy larger than the superconducting energy gap Δ itself. Since the AF coupling energy J, in $E_m = -J\mathbf{S}_1\mathbf{S}_2$, is of the order of 1000 K, it is interesting to note that a 3% Zn impurity level corresponds to ≈ 30 K, which is a magnitude similar to that of the superconducting energy gap $\Delta = 3k_BT_c = 60$ K in the Sr doped La$_2$CuO$_4$.

V. CONCLUSIONS

The present experimental frequency distribution in the μSR spectra can be well described with a model where the Cu moment perturbation is an oscillating function of the distance to the Zn atoms. We then find that the AF lattice in La$_2$CuO$_4$ is perturbed even at relatively large distances from Zn impurities.

If the pairing mechanism in these materials is of magnetic character it should be expected to be sensitive to magnetic inhomogenities. We find that the inhomogenity around each Zn atom is such that it can explain the decrease of superconducting carriers upon increase of Zn concentration in La-Sr-Cu-O, as determined by Nachumi.[25]

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